

2006 DOE/NETL ENVIRONMENTAL CONTROLS CONFERENCE

SESSION 2: TECHNIQUES FOR MANAGING SULFUR TRIOXIDE

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SO₃ INTRODUCTION/OVERVIEW

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PURPOSE OF INITIAL, 1998, ONLY PRIOR, DOE SO₃ CONFERENCE

- GUIDE NEW RESEARCH
- CHARACTERIZING THE SO₃ PROBLEM
 - ADDRESS SO₃ INTERFERENCES
 - ASSESS UNCERTAINTIES
 - INTEGRATE ACTION WITH EPA

[1998]

INITIAL, YEAR-1998, TRI REPORTING TO GOVERNMENT BY ELECTRIC UTILITIES

	<u>% OF TOTAL TOXINS</u>
HCl	50
SO ₃ /H ₂ SO ₄	25*
<u>Other</u>	<u>25</u>
Total	100

*Electric utility industry rivals chemical industry in annual mass amount of emission.

[1998]

ADDITIVE USE IN SO₃ ABATEMENT UPSTREAM OF RAW GAS PARTICULATE COLLECTOR

- Ammonia
- Magnesia

[1998]

DISTRIBUTION OF $\text{H}_2\text{SO}_4(\text{L})$, ACID MIST, THAT FORMS IN THE AIR PREHEATER

- Sorption by fly ash,
gasborne or deposited
- Flue gas exit stream
- Leakage to combustion
air stream

[1998]

INDICATION OF POTENTIAL PROBLEMS ABSENT SCR (AND ITS CATALYTIC, SO₂-TO-SO₃ CONVERSION)

- Average SO₃ concentration may be as high as 50 ppm, exceeding 3% of gross SO₂ content.
- With unique, high iron content, e.g. western Kentucky coal: up to 10% conversion of SO₂ to SO₃ occurs.

[1998]

UNIT-WIDE SO₂/SO₃ BEHAVIOR

- An increment of SO₃ generation occurs in the furnace.
- Temperature-dependent, catalyzed SO₂-to-SO₃ conversion occurs in the convective pass, reaching a maximum rate at 1,300°F (704°C) flue gas temperature.
- Rate of SO₃ formation by SCR, increasing SO₃ perhaps by 20± ppm, is greatest at 660-750°F (350-400°C) and above.
- Below 600°F (316°C) SO₃ hydrates to gaseous sulfuric acid: H₂SO₄(v).
- Condensation of H₂SO₄(v) occurs at and below the sulfuric acid dew point temperature, typically as high as 280°F (138°C).

[1998]

INFLUENCE OF SOOT BLOWING

- Low-temperature blowing/cleaning (1,100 to 1,600°F, i.e. 593 to 871°C), in removing deposits, increases the rate of SO_2 -to- SO_3 conversion due to tube-metal surface effect.
- However, (contrariwise), presence of such ash deposits, typically iron-oxide-laden, significantly increases SO_3 formation.

[1998]

INSIGHTS FROM MARCH, 1998, (MOST RECENT) DOE/FETC CONFERENCE ON SO₃

- A boiler model study showed that the condition of superheater tube surfaces radically influences catalytic SO₃ formation:
 - CLEAN: 20 ppm
 - MODERATELY FOULED: 70 ppm
 - HEAVILY FOULED: 32 ppm
- A large, high-SO₃, electric utility unit (without SCR) achieves 60% removal of SO₃ in the air preheater leading to its significant fouling (and derating). Across its exit cross-section, SO₃ varies laterally from 10 to 25 ppm.

[1998]

IMPACT ON AIR PREHEATER OF H_2SO_4 CONDENSATION IS EXACERBATED BY:

- Air to gas-side leakage
- Displacement of flue gas into air stream
- Enhancement of corrosion due to acid-wetted ash/salt deposit

[1998]

SCR CONCERNS RE SO₃ (AND NH₃)

- Design for 70% max. NO_x removal.
- Limit ammonia slip to 5 ppm.
- Avoid a potential SCR increase in SO₃ of 20 ppm.

[1998]

- If A Unit Has Significant, Air-Preheater-Related, SO₃ Problems, SCR Retrofitting Can Be Expected To Make The Situation Worse.
- If An Uncontrolled Unit Does Not Have Significant SO₃ Problems, Adequate SCR Retrofit System Design and Operation Should Not Lead To Increased Problems in Boiler System Performance or Maintenance.

CANDIDATE METHODS FOR MEASUREMENT OF SO₃ CONCENTRATION

- Controlled Condensation method
(CONSOL, Inc.)
- Severn Science, wet-chemistry,
continuous analyzer (Environmental
Energy Services)

[1998]

ACTION OF VANADIUM IN PETROLEUM-BASED RESIDUAL FUELS

- Residual Fuel Oil: 100 ppm SO_3 periodically
- Petroleum Coke: 158 ppm SO_3 peak value

OPERATION OF WET SCRUBBERS

- 0 to 70% $\text{SO}_3/\text{H}_2\text{SO}_4(\text{v})$ removal
- 0% $\text{H}_2\text{SO}_4(\text{L})$ removal
- Variable degree of conversion of $\text{H}_2\text{SO}_4(\text{v})$ to $\text{H}_2\text{SO}_4(\text{L})$, sulfuric acid mist aerosol, in the air preheater

[1998]

OPERATION OF DRY SCRUBBERS

- Non water-saturating design
- 98-99% $\text{SO}_3/\text{H}_2\text{SO}_4(\text{v})$ removal,
(greater than that of SO_2)

THRUST OF 2006 SO₃ CONFERENCE

- Emphasis on high-sulfur coal
- New data on rate of boiler SO₃ formation
- Broad benefits of depressing SO₃ concentration
- Wet ESP advancements: membrane type, new Siemens type
- Role of CFD Modeling

Con't →

- Sorbent technology/technique:
 - Lime
 - Trona
 - Sodium bisulfite/carbonate
 - Magnesium hydroxide
- Tie-in with mercury control
- Tie-in with SCR catalyst and air preheater operation
- Semi-continuous SO₃ emission monitoring